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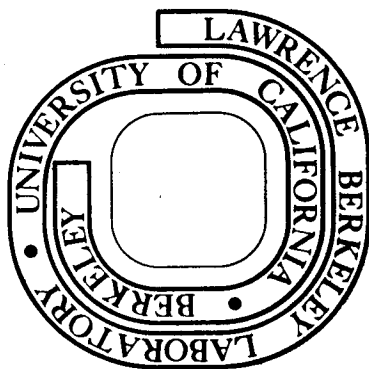
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POTENTIAL DIFFERENCES BETWEEN THE ALKALI
METALS AND THEIR AMALGAMS

Jacob Jorne^{*}

Department of Chemical Engineering and Material Sciences
Wayne State University, Detroit, Michigan 48202

and

Charles W. Tobias^{*}

Inorganic Materials Research Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering, University of California,
Berkeley, California 94720

^{*} Electrochemical Society Active Member

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rubidium amalgam, cesium amalgam, propylene carbonate.

Abstract

Potential differences have been measured between the alkali metals and their dilute amalgams in propylene carbonate solutions. The general cell $M(s) | M^+, X^-(PC) | M(Hg)$ has been used where $M = Li, Na, K, Rb,$ and $Cs,$ and $X^- = AlCl_4^-$ or PF_6^- . Some of the amalgam composition matched exactly the compositions used in the classical work of G. N. Lewis and good agreement was found. Additional data is presented for the potassium, rubidium and cesium amalgams.

Introduction

In the course of our studies on the thermodynamic properties (1,2) and the kinetic measurements (3) of the alkali metals in aluminum chloride-propylene carbonate (PC) solution, we have measured the potential difference between the alkali metals Li, Na, K, Rb and Cs and their respective dilute amalgams.

This is a report of a fragmentary nature which establishes the feasibility for a complete thermodynamic study of the alkali metal amalgams using propylene carbonate as a nonaqueous solvent.

In the present work we have confirmed some of the emf data of the early pioneering work of G. N. Lewis (4-7) and H. E. Bent (8, 12, 16) and their co-workers, and added some additional emf data for different amalgam concentrations. We feel that the additional and confirming data for potassium, rubidium and cesium are especially important because of the lack of data for these experimentally difficult systems.

Experimental

Alkali metal amalgams were prepared by weight from triple distilled mercury (Quicksilver Products Inc., San Francisco) and alkali metal ribbons (Li-Lithium Corp. of America, 99.9%; Na-Baker analyzed reagent; K - Mallinckrodt; Rb - Alfa Inorganic, $m2N^+$; Cs - United Mineral & Chemical Corp., New York, 99.8%). The amalgams were prepared inside a dry argon glove box (below 1 ppm water). The electrolytes were prepared from alkali metal chlorides (Mallinckrodt and Alfa Inorganic) and aluminum chloride (Baker, 99.2%) or sodium hexafluorophosphate (Alfa Inorganic, 99%) in propylene carbonate (Jefferson Chemical Corp., Houston, Texas). The distillation, purification and preparation of the solutions are discussed elsewhere and special precautions were necessary for the K, Rb and Cs cells (1,2,13).

Potentials were measured with a high impedance differential voltmeter (John,Fluke, model 887-A), accuracy ± 0.005 mV, which was calibrated against an Epply Laboratory low temperature coefficient standard cell.

The six compartment cells and the electrodes were described previously (1, 13, 14), and the potentials were measured between the alkali metals wires, or solidified pools of Rb and Cs in cup electrodes (1,3,13), and the corresponding alkali metal amalgams which were placed in cup electrodes. The measurements were repeated every 30 minutes for the first few hours. The potential drift during the first hour was less than 1 mV for most measurements. The potentials were extrapolated to zero time and represent average

0 0 0 0 3 8 0 1 4 0

values of at least 2 electrodes for each cell. The temperature was maintained at 25 ± 0.01 °C for all experiments. In the case of potassium the measurements were repeated for various temperatures up to 50 °C within ± 1 °C.

Results

The potential differences of the general cell:
 $M(s) | M^+, X^-(PC) | M(Hg)$ (where X^- is $AlCl_4^-$ or PF_6^-) were measured for $M = Li, Na, K, Rb$ and Cs . The results are summarized in Table 1 for various amalgam compositions.

Table 1

Potential Measurements of the Alkali Metal-Alkali Amalgams Cells

Cell	X mole fraction	Temp °C	E Volts
Li(s) LiAlCl ₄ (1M), PC Li(Hg)	0.01907	25	1.004
Na(s) NaAlCl ₄ (0.5M), PC Na(Hg)	0.01771	25	0.843
Na(s) NaPF ₆ (0.5M), PC Na(Hg)	0.02441	25	0.8319
Na(s) NaPF ₆ (0.5M), PC Na(Hg)	0.02982	25	0.7347 *
K(s) KAlCl ₄ (0.5M), PC K(Hg)	0.01126	25	1.0523
K(s) KAlCl ₄ (0.5M), PC K(Hg)	0.02271	25	1.0067
		29	1.013
		30	1.016
		43	1.057
		50	1.067
Rb(s) RbAlCl ₄ (0.5M), PC Rb(Hg)	0.005395	25	1.0766
Cs(s) CsAlCl ₄ (0.5M), PC Cs(Hg)	0.004551	25	1.107

* In disagreement with previous data, see text.

Discussion

The results of the present work can be compared with early results. The value of 1.004 V for $X_{Li}=0.01907$ Li(Hg) agrees with a value of 1.0037 V reported by Cogley and Butler (9). The first sodium amalgam measurement (0.843) V) satisfactorily agrees with the value of 0.8456 V reported by Lewis and Kraus (5) for the identical amalgam composition ($X_{Na} = 0.01771$). The second value of 0.8319 V agrees well with 0.830 V calculated after Mussini, Maina and Pagella (15). However the third value of 0.73470 V for $X_{Na} = 0.02982$ is significantly lower than the calculated value of 0.822 V (15). It is believed that the calculated value is the correct one because of the consistency of the data over the entire dilute range (15). It is quite possible that the present value is erroneous due to poisoning of the solid sodium in this particular measurement. The first two Na measurements agree well with the data reported by Hsueh and Bennion (11) and by Bent and Swift (12).

The potassium amalgam measurement of 1.0523 V is slightly higher than the value of 1.0481 V reported by Lewis and Keyes (6) for the same amalgam composition ($X_K = 0.01126$). The additional value of 1.0067 V for $X_K = 0.02271$ agrees with 1.01036 V calculated from the aqueous solution measurements of Bent and Gilfillan (16). The temperature coefficient of the emf of the $X_K = 0.02271$ amalgam cell was calculated from the data between 25 and 50°C, and the average value of $dE/dT = 0.0022 \pm 0.001$ V/°K

was obtained. The entropy of solution of potassium in $X_K = 0.02271$ amalgam is therefore

$$\Delta S = F(dE/dT) = (96580/4.186)(0.0022) = 50 \text{ cal/g mole } ^\circ K.$$

The emf value of 1.0766 V for $Rb(Hg)(X_{Rb} = 0.00539)$ agrees reasonably with the corresponding value of 1.0745 V reported by Lewis and Argo (7) for an identical amalgam composition, and with 1.077 V calculated from the aqueous solution measurements of Longhi, Mussini and Osimali (17).

The cesium amalgam mole fraction in the present work was 0.00455 and is higher than the composition of the cesium amalgam used by Bent et al (8), $X_{Cs} = 0.002827$; the value of 1.107 V obtained in the present work is indeed lower than the value of 1.121 V measured by Bent et al (8) for a more dilute amalgam, and agrees reasonably with the calculated value of 1.100 V after Mussini, Longhi and Riva (18).

The activity coefficients of cesium in its amalgams can now be calculated for the two measurements

$$\log \gamma_{Cs} = (F/2.303 RT) E - \log X_{Cs}$$

where the pure cesium has been chosen as the reference state, and the activity coefficients are based on the mole fraction X of the cesium in the amalgam.

For $X_{Cs} = 0.002827$	$\log \gamma_{Cs} = -16.4$, and for
$X_{Cs} = 0.00454$	$\log \gamma_{Cs} = -16.4$.

The potentials were measured every 30 minutes for the first few hours and extrapolated to zero time. The time dependent potential drift is due to the reactivity of the alkali metal amalgams,

especially lithium amalgam, toward PC. Doucek, Jansta and Říha (19) report that active lithium reacts with PC freed from impurities with the formation of Li_2CO_3 and propylene. They prove that the Li_2CO_3 layer passivates the solid lithium surface. The decomposition of lithium amalgam in highly pure PC (water content was lower than 0.01 ppm) is even stronger due to surface renewal of the amalgam. The rate of PC decomposition by the alkali metal amalgams decreases sharply in the order $\text{Li} > \text{Na} > \text{K}$. (19) The presence of traces of water in the electrolytic solution (45 ppm) decreases the PC decomposition by the Li-Hg amalgam considerably as it is believed that the amalgam surface is blocked by LiOH (19). Dey (20) also speculates on the film formation in Li-PC systems, and Scarr (21) predicts PC decomposition by Li from thermodynamic considerations.

In the present investigation, the water content was mostly 10 ppm and in some cases up to 50 ppm, and therefore it is quite possible that the protective layer slowed down the chemical decomposition, especially in the Li amalgam case. Similar behavior of potential drift in nonaqueous cells was observed in PC (1,22) DMSO (23,24), DMF (25) and N-MF (26). True cell potentials were obtained by extrapolating to zero time in formamide (27,28). The general agreement with the previous reliable data justifies the extrapolation procedure in the present work.

In conclusion, this fragmentary study establishes the feasibility of using propylene carbonate for thermodynamic measurements of the alkali metal amalgams.

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